F(7)	0.0484 (7)	0.2704 (14)	0.1984 (3)	0.169 (5)
F(8)	0.1154 (6)	0.5331 (12)	0.1688 (4)	0.142 (4)
F(9)	−0.0181 (6)	0.3792 (13)	0.1217 (3)	0.143 (4)
F(10)	0.2162 (5)	−0.3761 (8)	0.0532 (3)	0.096 (3)
F(11)	0.2402 (6)	−0.2066 (10)	−0.0195 (3)	0.103 (3)
F(12)	0.0653 (5)	−0.2054 (9)	0.0188 (3)	0.104 (3)
O(1)	0.5896 (5)	−0.0043 (8)	0.1110 (2)	0.044 (2)
O(2)	0.5306 (5)	0.3248 (8)	0.1754 (2)	0.045 (2)
O(3)	0.2924 (5)	0.2937 (8)	0.1415 (2)	0.049 (2)
O(4)	0.3501 (5)	−0.0234 (8)	0.0710 (2)	0.048 (2)
N(1)	0.4764 (5)	0.3744 (10)	0.0449 (2)	0.038 (3)
C(1)	0.6859 (8)	0.0008 (12)	0.1442 (4)	0.043 (3)
C(2)	0.7119 (8)	0.1277 (13)	0.1877 (3)	0.050 (3)
C(3)	0.6327 (9)	0.2784 (13)	0.2006 (3)	0.047 (4)
C(4)	0.7832 (10)	−0.1578 (16)	0.1322 (5)	0.066 (4)
C(5)	0.6640 (11)	0.4042 (19)	0.2519 (5)	0.083 (5)
C(6)	0.1850 (9)	0.2410 (13)	0.1264 (3)	0.045 (3)
C(7)	0.1490 (8)	0.0866 (13)	0.0899 (4)	0.051 (3)
C(8)	0.2341 (9)	−0.0342 (13)	0.0656 (3)	0.044 (3)
C(9)	0.0808 (10)	0.3608 (20)	0.1530 (5)	0.078 (5)
C(10)	0.1855 (10)	−0.2064 (16)	0.0295 (5)	0.066 (5)
C(11)	0.5066 (7)	0.5632 (13)	0.0523 (3)	0.043 (3)
C(12)	0.4693 (7)	0.3124 (11)	−0.0082 (4)	0.041 (3)

Table 2. *Geometric parameters* (Å, °)

Cu(1)—O(1)	1.963 (5)	Cu(1)—O(2)	1.938 (5)
Cu(1)—O(3)	1.956 (6)	Cu(1)—O(4)	1.946 (5)
Cu(1)—N(1)	2.248 (6)	O(1)—C(1)	1.267 (10)
O(2)—C(3)	1.263 (10)	O(3)—C(6)	1.243 (11)
O(4)—C(8)	1.249 (11)	N(1)—C(11)	1.327 (11)
N(1)—C(12)	1.326 (10)	C(1)—C(2)	1.362 (12)
C(1)—C(4)	1.536 (13)	C(2)—C(3)	1.373 (12)
C(3)—C(5)	1.508 (15)	C(6)—C(7)	1.398 (12)
C(6)—C(9)	1.546 (15)	C(7)—C(8)	1.377 (13)
C(8)—C(10)	1.521 (13)	C(11)—C(12*A*)	1.378 (12)
C(12)—C(11*A*)	1.378 (12)		
O(1)—Cu(1)—O(2)	91.3 (2)	O(1)—Cu(1)—O(3)	163.9 (2)
O(2)—Cu(1)—O(3)	85.9 (2)	O(1)—Cu(1)—O(4)	87.4 (2)
O(2)—Cu(1)—O(4)	168.5 (2)	O(3)—Cu(1)—O(4)	92.1 (2)
O(1)—Cu(1)—N(1)	99.1 (2)	O(2)—Cu(1)—N(1)	96.8 (2)
O(3)—Cu(1)—N(1)	97.0 (2)	O(4)—Cu(1)—N(1)	94.7 (2)
Cu(1)—O(1)—C(1)	124.5 (5)	Cu(1)—O(2)—C(3)	125.0 (5)
Cu(1)—O(3)—C(6)	124.6 (5)	Cu(1)—O(4)—C(8)	125.7 (5)
Cu(1)—N(1)—C(11)	122.8 (5)	Cu(1)—N(1)—C(12)	121.6 (5)
C(11)—N(1)—C(12)	115.6 (7)	O(1)—C(1)—C(2)	128.0 (8)
O(1)—C(1)—C(4)	114.2 (7)	C(2)—C(1)—C(4)	117.8 (8)
C(1)—C(2)—C(3)	122.1 (8)	O(2)—C(3)—C(2)	127.9 (8)
O(2)—C(3)—C(5)	113.2 (8)	C(2)—C(3)—C(5)	118.9 (8)
O(3)—C(6)—C(7)	128.0 (8)	O(3)—C(6)—C(9)	114.5 (8)
C(7)—C(6)—C(9)	117.5 (8)	C(6)—C(7)—C(8)	122.3 (8)
O(4)—C(8)—C(7)	127.2 (8)	O(4)—C(8)—C(10)	114.5 (8)
C(7)—C(8)—C(10)	118.2 (8)	N(1)—C(11)—C(12*A*)	122.8 (7)
N(1)—C(12)—C(11*A*)	121.6 (7)		

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and geometry involving fluorine have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71112 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1035]

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The Monopotassium Salt of the Ligand of a Ziegler–Natta Catalyst

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Abstract

The anion of dipotassium (*tert*-butylamino)-dimethyl(tetramethylcyclopentadienyl)silanediide can coordinate to transition metals to form precursors for single-component Ziegler–Natta polymerization catalysts. The related monoanion derivative potassium (*tert*-butylamino)dimethyl(tetramethylcyclopentadienyl)silanide tetrahydrofuran solvate has been isolated as the first crystalline salt of this important ligand family. The tetramethylcyclopentadienyl group in the crystal has a potassium ion on each face, 2.8 Å from the center of the five-membered ring; each K atom is bonded to two rings and one tetrahydrofuran solvent molecule.

Comment

The organoscandium complexes $[\{(C_5Me_4)SiMe_2(NCMe_3)\}ScR]_2(PMe_3)_x$ (R = H, $CH_2CH_2CH_3$; x = 2, 0) are the first compounds which catalyze the homogeneous Ziegler–Natta polymerization of

† Contribution No. 8735

α-olefins without activation by a co-catalyst, such as alkylaluminium reagents or 'methylaluminoxane' (Shapiro, Bunel, Schaefer & Bercaw, 1990). The synthesis of these complexes is hampered by retention of nonstoichiometric amounts of LiCl and tetrahydrofuran (THF) in the precursor $[\{(C_5Me_4)SiMe_2(NCMe_3)\}ScCl]_x$–$(LiCl)_y(THF)_z$, formed by treatment of $ScCl_3(THF)_3$ with the dilithium reagent $Li_2[(C_5Me_4)SiMe_2(NCMe_3)]$ in toluene. We have found that the dipotassium reagent $K_2[(C_5Me_4)SiMe_2(NCMe_3)]$ reacts with $ScCl_3(THF)_3$ in THF yielding cleanly $[\{(C_5Me_4)SiMe_2(NCMe_3)\}ScCl](THF)$, which is a suitable precursor for the preparation of the catalytic complexes (Cotter & Bercaw, 1993). However, the preparation of $K_2[(C_5Me_4)SiMe_2(NCMe_3)]$ itself is problematic; frequently the monopotassium derivative $K[(C_5Me_4)SiMe_2\{N(H)CMe_3\}]$ is obtained. In contrast to the lithium derivative, these potassium salts are highly crystalline and soluble in warm donor solvents.

In a dry box, $H_2[(C_5Me_4)SiMe_2(NCMe_3)]$ (26.06 g, 0.104 mol) was dissolved in THF (250 ml). KH (8.30 g, 0.207 mol) was added to the solution. The resulting slurry was refluxed overnight under argon on a Schlenk line. THF was removed *in vacuo*. The crude solid product was transferred to a large frit assembly and rinsed with petroleum ether, leaving behind a white powdery solid. A portion (10.81 g) of this material was purified *via* Soxlet extraction in THF, with a great reduction in yield (5.48 g). Elemental analysis of this material is consistent with the formulation $K[(C_5Me_4)SiMe_2\{N(H)CMe_3\}]$ [calc. (found): C 62.87 (61.53); H 9.75 (9.52); N 4.84% (4.99%)]. Colorless rod-shaped crystals of this material were obtained by slow cooling of a hot THF solution and were placed in capillaries in a dry box. Outside a sealed environment, these crystals are sensitive to solvent loss, visibly losing crystallinity within minutes of their removal from the crystallization flask.

The asymmetric unit of this structure is shown in Fig. 1. Bond distances and angles are generally within normal ranges; the Si—C(cyclopentadienyl) bond is 1.827 (4) Å, much shorter than the Si—CH_3 bonds [average 1.873 (6) Å, compared to 1.86 Å expected (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987)] and much shorter than others we have measured recently [average 1.867 (14) Å (Marsh, Schaefer, Coughlin & Bercaw, 1992; Schaefer, Köhn & Bercaw, 1992)]. The cyclopentadienyl ring shows evidence of localized double bonds, in that the C—C bonds to C1 average 1.426 (6) Å, C2—C3 and C4—C5 average 1.385 (16) and C3—C4 is 1.410 (7) Å. Thus, C1 has less double-bond character in its Cp ring bonds and could form a stronger bond to Si, as observed.

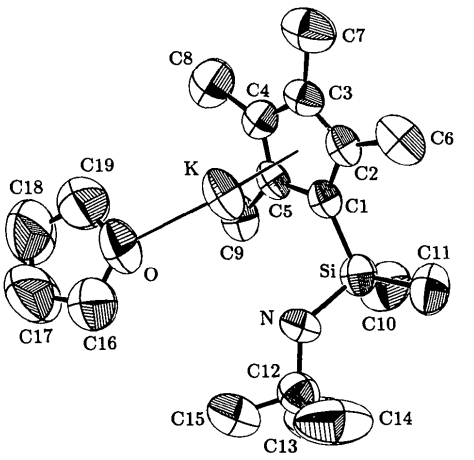

Fig. 1. An *ORTEP* drawing with 50% probability ellipsoids of one asymmetric unit showing the numbering system used. H atoms are not shown.

The ligand molecules are joined in chains by the potassium ions (Fig. 2). Each potassium ion is bonded to two cyclopentadienyl groups, and each cyclopentadienyl ring has a potassium ion on each side of it. The centroid of the five ring-carbon atoms in the cyclopentadienyl group, Cp*, is 2.81 Å from K^+ on one side and 2.78 Å from another K^+ on the other. The tetrahydrofuran solvent is attached to the potassium ion through oxygen: K—O 2.762 (5) Å. The two Cp* centers and one oxygen form a planar array about K^+, with angles Cp*—K—O 108.4 and 106.1°; Cp*—K—Cp'* is 145.5°. The angle K—Cp*—K′ is 176.2°, with the plane of the cyclopentadienyl group nearly perpendicular to the K—K′ vector (the primes indicate a transformation by the twofold screw axis).

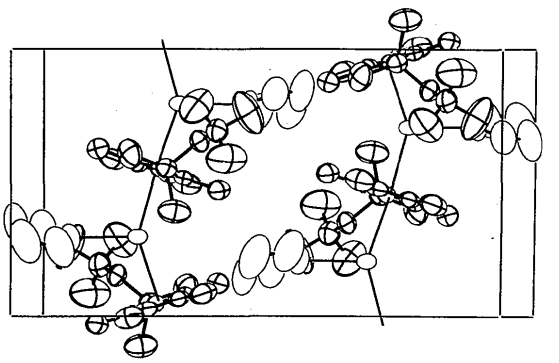

Fig. 2. An *ORTEP* drawing of the contents of a unit cell, with a unit cell outlined. The view is perpendicular to the *bc* plane, with the *c* axis horizontal. The potassium ion and the tetrahydrofuran molecule are shown without quadrant outlining. H atoms are not shown.

Experimental

Crystal data

$K^+.C_{15}H_{28}NSi^-.C_4H_8O$
M_r = 361.68
Monoclinic
$P2_1/n$
a = 10.799 (3) Å
b = 10.676 (5) Å
c = 19.894 (4) Å
β = 97.13 (2)°
V = 2275.8 (13) Å^3
Z = 4
D_x = 1.06 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 6–17°
μ = 0.29 mm^{-1}
T = 294 K
Irregular parallelepiped
1.22 × 0.44 × 0.35 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
θ–2θ scans
Absorption correction: none
4870 measured reflections
2116 independent reflections
2116 observed reflections
R_{int} = 0.026
θ_{max} = 20°
h = 0 → 10
k = −10 → 10
l = −19 → 19
3 standard reflections
frequency: 150 min
intensity variation: within counting statistics

Refinement

Refinement on F^2
Final R = 0.064
wR = 0.013
S = 3.36
2116 reflections
212 parameters
H-atom parameters not refined (except NH)
$w = 1/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{max}$ = 0.13
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}
Atomic scattering factors from Cromer & Waber (1974)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
K	0.7457 (1)	0.2949 (1)	0.7913 (1)	0.0821 (4)
C1	0.8612 (4)	0.0482 (4)	0.7601 (2)	0.0583 (12)
C2	0.7919 (6)	0.0801 (4)	0.6969 (2)	0.0631 (15)
C3	0.6665 (6)	0.0659 (4)	0.7006 (3)	0.0670 (16)
C4	0.6509 (5)	0.0243 (4)	0.7663 (3)	0.0676 (16)
C5	0.7696 (5)	0.0134 (4)	0.8026 (2)	0.0605 (14)
C6	0.8433 (5)	0.1234 (4)	0.6334 (2)	0.0987 (17)
C7	0.5606 (6)	0.0843 (4)	0.6440 (3)	0.1129 (19)
C8	0.5292 (6)	−0.0058 (5)	0.7919 (3)	0.1142 (19)
C9	0.7970 (5)	−0.0306 (4)	0.8754 (2)	0.0886 (15)
Si	1.0298 (1)	0.0507 (1)	0.7850 (1)	0.0757 (4)
N	1.0536 (5)	0.1524 (4)	0.8530 (2)	0.0765 (13)
C10	1.0895 (5)	−0.1109 (5)	0.8051 (3)	0.129 (2)
C11	1.1252 (5)	0.1032 (6)	0.7174 (3)	0.1172 (19)
C12	1.1652 (5)	0.1926 (5)	0.8970 (3)	0.0882 (17)
C13	1.2500 (7)	0.0863 (7)	0.9211 (4)	0.202 (3)
C14	1.2376 (7)	0.2854 (8)	0.8598 (4)	0.189 (3)
C15	1.1281 (7)	0.2597 (9)	0.9566 (4)	0.207 (4)
O	0.7190 (6)	0.2918 (4)	0.9276 (2)	0.1190 (15)
C16	0.7863 (7)	0.3309 (7)	0.9877 (5)	0.149 (3)
C17	0.7038 (12)	0.3424 (10)	1.0361 (4)	0.201 (4)
C18	0.5925 (10)	0.2807 (10)	1.0100 (6)	0.217 (4)
C19	0.6030 (9)	0.2590 (9)	0.9413 (5)	0.184 (4)

Table 2. *Geometric parameters* (Å, °)

Cp* is the centroid of the five C atoms of the cyclopentadienyl ring.

K—Cp*	2.808	Si—C10	1.867 (6)
K—O	2.762 (5)	Si—C11	1.878 (6)
C1—C2	1.423 (6)	Si—N	1.729 (4)
C1—C5	1.428 (6)	N—C12	1.463 (7)
C2—C3	1.373 (7)	C12—C13	1.499 (10)
C2—C6	1.514 (7)	C12—C14	1.512 (10)
C3—C4	1.410 (7)	C12—C15	1.483 (10)
C3—C7	1.515 (7)	O—C16	1.385 (9)
C4—C5	1.396 (7)	O—C19	1.361 (11)
C4—C8	1.502 (8)	C16—C17	1.396 (13)
C5—C9	1.515 (7)	C17—C18	1.412 (15)
Si—C1	1.827 (4)	C18—C19	1.405 (15)
Cp*—K—O	108.3	C1—Si—N	105.5 (2)
C5—C1—C2	105.0 (4)	C10—Si—C11	102.9 (3)
C3—C2—C1	109.9 (4)	C10—Si—N	113.5 (2)
C6—C2—C1	127.1 (4)	C11—Si—N	109.4 (2)
C6—C2—C3	123.0 (4)	Si—N—C12	133.1 (4)
C4—C3—C2	108.5 (4)	C13—C12—N	113.2 (5)
C7—C3—C2	127.2 (5)	C14—C12—N	109.7 (5)
C7—C3—C4	124.3 (5)	C15—C12—N	109.6 (5)
C5—C4—C3	107.4 (4)	C14—C12—C13	108.7 (5)
C8—C4—C3	126.3 (5)	C15—C12—C13	109.0 (6)
C8—C4—C5	126.3 (5)	C15—C12—C14	106.4 (6)
C4—C5—C1	109.3 (4)	C19—O—C16	107.6 (6)
C9—C5—C1	125.3 (4)	C17—C16—O	108.1 (7)
C9—C5—C4	125.4 (4)	C18—C17—C16	107.0 (9)
C1—Si—C10	110.5 (2)	C19—C18—C17	105.5 (9)
C1—Si—C11	115.3 (2)	C18—C19—O	109.9 (8)

Before averaging, 41 reflections were deleted from the data set because of shutter problems with the diffractometer. The goodness-of-fit for merging 1967 multiply-measured reflections was 1.25. The weights and variances $[\sigma^2(F_o^2)]$ were derived from counting statistics plus an additional term, $(0.014\bar{I})^2$; variances of the merged data were obtained by propagation of error plus another additional term, $(0.014I)^2$. Values for f' were taken from Cromer (1974). The programs used were those of the *CRYM Crystallographic Computing System* (Duchamp, 1964) and *ORTEP* (Johnson, 1976). H atoms on C were placed by calculation (C—H 0.95 Å) assuming staggered configurations except on the Cp* group, where the atoms were placed at idealized positions based on difference maps calculated in the expected planes. H atoms were included at fixed positions, with B values corresponding to 1.2 times the isotropic equivalent U_{ij} value of the bonded atoms. They were repositioned once near the end of the refinement. The H atom on N was located in a difference map and its parameters were refined.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71110 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1051]

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A Second Crystal Form of Bis-μ-[bis(dimethylphosphino)methane]-bis(tricarbonylrhenium)(*Re—Re*), $Re_2(dmpm)_2(CO)_6$

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Abstract

The second crystalline form, (II), of the title compound has the same space group ($P2_1/n$) as form (I) of known structure [Milder, Castellani, Weakley, Tyler, Miskowski, & Stiegman (1990). *J. Phys. Chem.* **94**, 6599–6603] but has a different packing. There is no disorder in (II) [in contrast to (I)] and the Re—Re bond length is significantly longer [3.126 (1) *versus* 3.105 (1) Å] despite the smaller (*ca* 1.3%) molecular volume.

Comment

The data crystal of form (II) came from the air-stable batch which earlier (Milder *et al.*, 1990) had afforded the crystal of form (I). Both forms have space group $P2_1/n$ with two molecules per cell, but they clearly differ in molecular packing. The unit cell of (II), and hence the molecular volume, is 1.3% smaller. Accurately centrosymmetric $Re_2(dmpm)_2(CO)_6$ moelcules with Re—Re bonds, bridging dmpm ligands, *trans* P—Re—P geometry, and generally similar dimensions, are present in both forms. The principal points of difference are as follows. The Re—Re bond in (II) [3.126 (1) Å] is significantly longer than in (I) [3.105 (1) Å]. Alternative positions for three of the five dmpm C atoms are discernible in (I), but (II) is free from disorder, a feature that accounts for the more efficient molecular packing in (II) and the fact that the C—P—C angles lie within the range 100.9–104.0 (6)° compared with 86–116 (1)° for the major conformer in (I).

A series of events led us to determine the unit cells of 20 crystals from a stable batch. Eight proved to be of form (II). The two forms, both amber prisms, cannot be readily distinguished under the polarizing microscope. We think it is unlikely that most workers routinely find the cell dimensions for several crystals from an apparently homogeneous sample if the first crystal proves suitable for data collection. We feel, therefore, that the presence of two crystalline forms in one batch may be more common than is generally supposed.

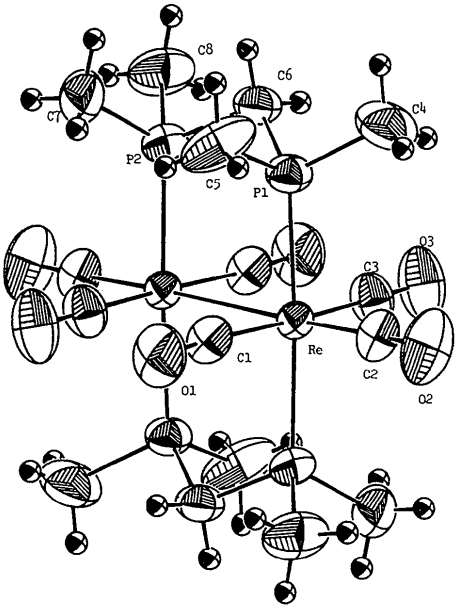

Fig. 1. View of the $Re_2(dmpm)_2(CO)_6$ molecule showing thermal ellipsoids.

Experimental

Crystal data

$[Re_2(C_5H_{14}P_2)_2(CO)_6]$
M_r = 812.70
Monoclinic
$P2_1/n$
a = 9.938 (2) Å
b = 8.579 (3) Å
c = 14.783 (3) Å
β = 93.53 (2)°
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 11.5–16.1°
μ = 10.0 mm^{-1}
T = 297 K
Prism
0.30 × 0.25 × 0.15 mm